

REMENDABLE POLYMERIC MATERIALS USING REVERSIBLE COVALENT BONDS

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ABSTRACT

Materials that can recover mechanical properties following failure offer increased safety and service life. Moreover, successful development of such systems would reduce factors of safety required in design thus reducing weight. Inspiration for remendable materials comes from nature where the ability to heal is a characteristic of living organisms and a prime example of autonomy. The development of self-healing polymeric material systems could therefore enable new multifunctional composite systems used in military applications. Two approaches for healing polymer networks have captured much attention. In one method, polymer networks are made to self-heal by adding particles filled with uncured resin. The resin held within the particles is released upon crack formation and cures to mend the damage. The other mechanism for healing relies on inherent reversibility of bonds found designed into polymer networks. The work to be presented is part of the Drexel-ARL Army Materials Center of Excellence (MCOE) program for polymers.

Our approach to design self-healing composites combines advantages of healing via encapsulation and healing via reversible bonds. Incorporation of a healing agent allows for crack healing while maintaining the desirable physical and mechanical properties of the base thermoset. Reversible bonding of the healing agent provides the ability to crack heal cracks multiple times.

We report on the development of two healing systems for epoxy-amine thermosets based on the thermoreversible Diels-Alder reaction of furan and maleimide. In one, crack healing of a traditional epoxy-amine thermoset is induced by thermally reversible crosslinking of a secondary phase. The secondary phase can be in the form of microspheres or fibrous mats. In the other, furan functionalization of an epoxy-amine thermoset allows for *in-situ* crack healing of this thermoset with a bismaleimide solution. Both phenomena occur at room temperature and minimal pressure and significant load recovery is possible multiple times in a given location.

In both methods significant strength recovery is observed. In the second close to complete recovery is observed. In this case strength recovery is postulated to be the result of both physical and chemical bonding across the crack surface. Physical bonding is caused by solvent-mediated swelling and subsequent interlocking of crack surfaces, while chemical bonding results from the Diels-Alder reaction of furan and maleimide. This form of the Diels-Alder reaction is reversible, forming a ring structure at room temperature and reforming the respective diene and dienophile between 60 and 90°C.

The degree of strength recovery is linked to a detailed kinetic analysis of the reversible reaction obtained using near IR spectroscopy. Moreover, the polymer network design is based on this analysis and takes into account intrinsic kinetics as well as diffusion limitations that limit the approach to equilibrium compositions at processing and healing temperatures.

1. INTRODUCTION

Materials that can repair cracks and recover from mechanical failure are desirable for a number of military applications. Because remendable materials both repair and prevent the propagation of cracks on the micro scale, they offer the potential for increased durability, safety, and cost efficiency for many applications. Two approaches for healing polymer networks have captured much attention. In one method, polymer networks are made to self-heal by adding microcapsules filled with uncured resin (Blaiszik et al. 2008; Brown et al. 2005; Kessler et al. 2003; Li et al. 2007; Liu et al. 2007; White et al. 2001; Yin et al. 2008). Upon fracture the microcapsules rupture releasing the resin, which hardens to heal the crack. The other method relies on the inherent reversibility of bonds designed into a polymer network (Bergman; Wudl 2008; Canary; Stevens 1992; Chen et al. 2002; Chujo et al. 1990; Cordier et al. 2008; Craven 1969; Fall; Ward 2001; Gheneim et al. 2002; Kalista; Ward 2007; Kavitha; Singha 2007; Kennedy; Castner 1979; Liu; Chen 2007; Liu et al. 2006; Murphy et al. 2008; Nijenhuis 1997; Salamone et al. 1988; Sijbesma 1997; Varley; van der Zwaag 2007). The reversible nature of these linkages allows for network remodeling at the

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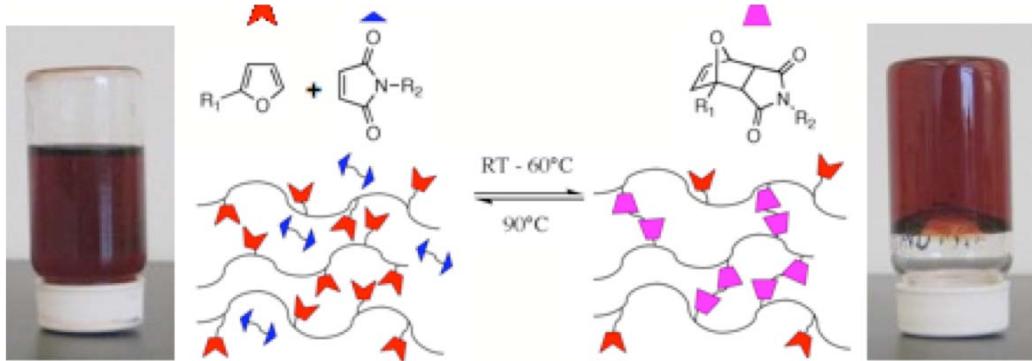


Figure 1. Thermoreversible crosslinking gel: crosslinking chemistry (top center), a schematic of the reversible network (bottom center), and photographs showing liquid (left) and gel

damaged site. We have employed a composite approach to self-healing that combines many advantages of healing via encapsulation and healing via reversible bonds. This methodology allows for localized healing by including a secondary phase that induces healing through thermoreversible bonding while maintaining the mechanical and physical properties of the base thermoset.

We report on the development of two healing systems for epoxy-amine thermosets based on the thermoreversible Diels-Alder reaction of furan and maleimide. One system consists of a reversibly crosslinking network that can heal a traditional epoxy-amine thermoset. The ability to heal was evaluated by *in situ* crack healing of modified compact tension (CT) specimens. In the other, furan functionalization of an epoxy-amine thermoset allows for bonding of this thermoset with a bismaleimide solution. Both systems heal at room temperature and minimal pressure. Additionally, significant load recovery is possible multiple times in a given location.

Healing with a secondary agent allows for crack healing while maintaining the desirable physical and mechanical properties of the base thermoset. Reversible bonding of the healing agent results in a material that exhibits the mobility of a linear polymer at increased temperatures and the mechanical properties of a crosslinked polymer at ambient conditions. The reversible healing agent also provides the ability to heal multiple times.

The Diels-Alder reaction is a cycloaddition of a diene and a dienophile. This reaction forms a ring structure at room temperature and reforms the respective diene (furan) and dienophile (maleimide) between 60 and 90°C.

2. MATERIALS

Furfuryl amine (FA), 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI), furfuryl glycidyl ether

(FGE), phenyl glycidyl ether (PGE), and *N,N*-dimethylformamide DMF were obtained from Sigma-Aldrich. EPON 828, a Diglycidyl ether of bisphenol-A (DGEBA) with EEW=185-192 was obtained from Miller-Stephenson. 4,4'-methylenebiscyclohexanamine (PACM) was obtained from Air Products. All materials were used as received.

3. EXPERIMENTAL PROCEDURE

3.1 Synthesis of a Reversibly Crosslinking Gel

The crosslinks of this gel are based on the Diels-Alder reaction between maleimide groups on a bismaleimide and pendant furans on a linear polymer, similar to many other reversibly crosslinking networks (Craven 1969; Gheneim et al. 2002; Goiti et al. 2003; Gousse et al. 1998; Imai et al. 2000; Laita et al. 1997). A schematic representation of this network is shown in Figure 1 with maleimide moieties as triangles, furan moieties as notched trapezoids and Diels-Alder adducts as trapezoids. Also shown in Figure 1 are the Diels-Alder reaction and pictures of vials containing the liquid system at 90°C and the gel at room temperature (RT).

The linear polymer was a copolymer of FA and DGEBA. Stoichiometric amounts of FA and DGEBA were mixed to form a 15 wt.% solution in DMF which was reacted at 90°C for 30 hours. Crosslinking occurred by adding a stoichiometric amount of BMI to the linear polymer solution at room temperature and allowing sufficient time for reaction.

At room temperature the crosslinked network is a DMF-swollen gel. However, after approximately 20 minutes at 90°C a sufficient number of crosslinks are reversed so that the system liquifies and forms a polymer-bismaleimide solution in DMF. Upon cooling to ambient temperature a gel was observed to form after approximately 13 hours.

3.2 Synthesis of a Furan-Functionalized Network

Incorporation of furan groups in the polymer network was achieved through modification of an epoxy-amine network. DGEBA reacts via step growth polymerization with 4,4'-methylenebiscyclohexanamine PACM, an aliphatic diamine. This system was modified by substituting DGEBA with a stoichiometric amount of furfuryl glycidyl ether (FGE), a furan-containing epoxy. In addition to providing furan functionality, the use of FGE as a comonomer allows for tailoring of T_g . The dependence of T_g on FGE loading is shown in Figure 2. T_g values were obtained from heating at a rate of $10^\circ\text{C min}^{-1}$ with a TA Instruments Differential Scanning Calorimeter (DSC Q2000).

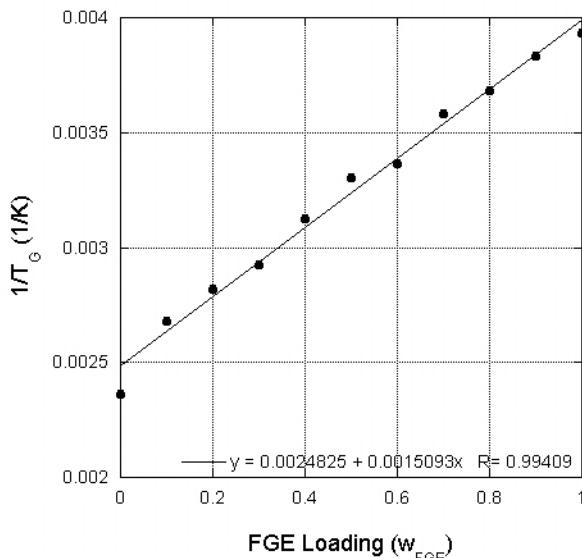


Figure 2. T_g -dependence on FGE content.

DGEBA, FGE, and PACM were mixed in stoichiometric amounts with a FGE loading of $w_{FGE}=0.4$, where w_{FGE} is the fraction by weight of epoxide groups contributed by FGE. The system was cured 2 hours at 60°C and 2 hours at 90°C to ensure complete cure. Full reaction was confirmed with DSC.

3.3 Compact Tension Testing

The reversibly crosslinked network was used as a healing agent for an epoxy-amine thermoset. The ability of the reversibly crosslinked gel to function as a healing agent was evaluated by measuring *in-situ* crack healing of modified CT specimens of DGEBA and PACM. DGEBA and PACM were mixed in stoichiometric amounts and cured for 2 hours at 85°C and 2 hours at 165°C to ensure complete cure and a T_g of 160°C (G. R. Palmese 1992). For comparison, base-line healing studies were also conducted with no healing agent, linear polymer solution in DMF, and pure DMF. Before injection into the crack, the healing agent (DMF, linear polymer solution, or

reversibly crosslinked polymer solution) was heated at 90°C for 1 hour.

Geometry and test procedure of CT specimens are explained in greater detail elsewhere (Chen et al. 2003). Specimens were loaded at a rate of 0.1 mm min^{-1} in tension until failure. Once CT specimens were fractured, the crack was filled with $10 \mu\text{L}$ of healing agent and left to heal at room temperature under minimal pressure for 12 hours. After healing, specimens were loaded to failure to determine load recovery for heal 1. For subsequent healing cycles, specimens were heated at 90°C for 1 hour under no pressure, and healed for 12 hours at room temperature under minimal pressure. This testing procedure was repeated until specimens no longer recovered load following healing. Minimal pressure ($\sim 4.7 \text{ kPa}$) during healing was provided by placing a 240 g plate on top of specimens.

4. RESULTS AND DISCUSSION

4.1 Crack Healing with Reversibly Crosslinked Network

Results for load recovery are presented in Figure 3. Linear polymer and crosslinked polymer are labeled as LP and CLP, respectively. Healing values for DMF as the healing agent and systems with no healing agent are not shown because the specimens did not recover any load.

Load recoveries and healing efficiencies using the crosslinked polymer as a healing agent significantly outperform the linear polymer healing agent for the first heal. The linear polymer recovered an average load of $6.3 \pm 1.2 \text{ N}$ ($9.6 \pm 3.1\%$ healing efficiency), as compared to $25 \pm 3.9 \text{ N}$ ($37 \pm 8.3\%$) for the crosslinked polymer healing agent.

The inability of DMF to heal DGEBA-PACM runs counter to the work of Caruso et al. who observed solvent-promoted healing of another epoxy-amine network (Caruso et al. 2007). The difference in behavior could be due to the much higher crosslink density and T_g of our system.

4.2 Bonding with BMI Solutions

Specimens with $w_{FGE}=0.4$ were polished using sandpaper of different grits and then “glued” together using $\sim 0.02 \text{ g}$ of a high concentration BMI solution in DMF. Surface conditions play a significant role in healing. While specimens polished using 1600 grit sandpaper were bonded together effectively, specimens polished using 120 grit sandpaper did not adhere to one another. Additionally, specimens of a furan-free polymer network with the same crosslink density as $w_{FGE}=0.4$ prepared with phenyl glycidyl ether (PGE), DGEBA, and

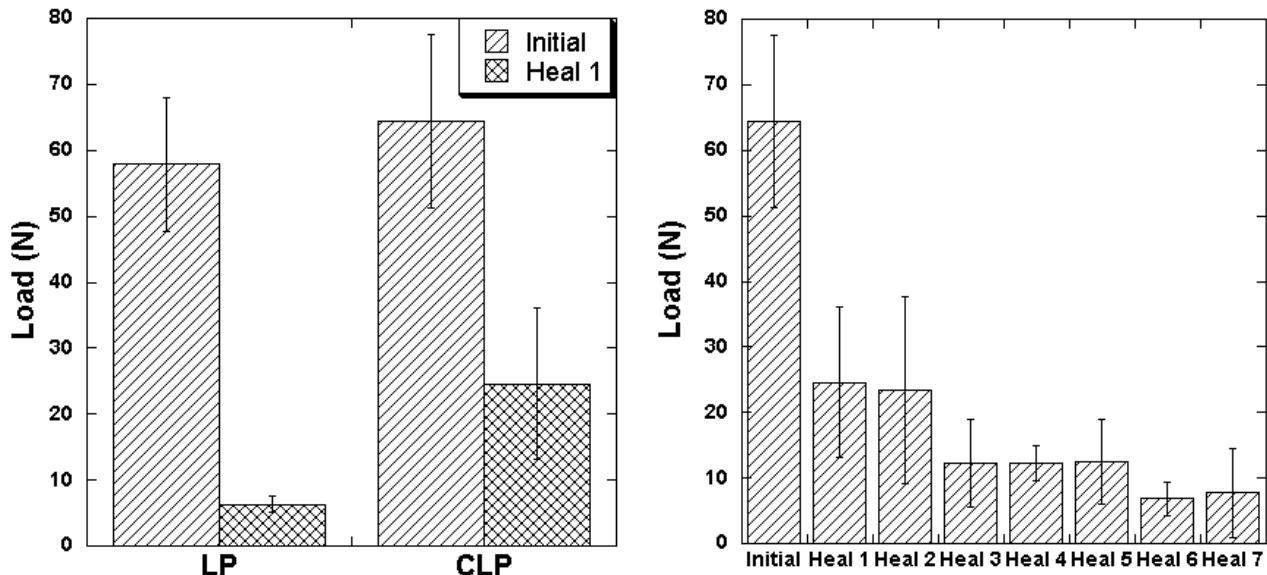


Fig. 3 Load recovery for first heals for linear (LP) and crosslinked (CLP) healing agents (left) and subsequent heals for CLP (right). Error bars indicate standard deviations.

PACM did not bond using the BMI solution regardless of surface conditions. No system bonded when DMF was used as the glue.

We proposed that the primary healing mechanism is covalent bond formation across the crack surface. At room temperature furans and maleimides react via cycloaddition to form Diels-Alder adducts. In this system, BMI reacts with surface furans. If the distance between surfaces is less than the length of a BMI molecule, bonding can occur. Additional mechanisms, such as those related to the swelling behavior or T_g of the material may also play a role in healing.

5. CONCLUSIONS

We have developed a novel healing system based on the Diels-Alder reaction that allows a traditional epoxy-amine thermoset to recover mechanical properties multiple times following failure in the same location. In future work, methods of incorporating the thermoreversible gel into epoxy-amine thermosets will be investigated.

Future work in healing furan-functionalized networks will focus on characterizing healing using modified CT specimens as well as developing methods of incorporating BMI solutions in composites. Possibilities include hollow glass fibers and polymer microcapsules. Additionally, we plan to improve our understanding of the mechanisms of healing for this healing system so as to create materials with optimized healing abilities. Topics of interest include quantifying the effects of T_g , solvent, BMI concentration, and BMI structure on healing.

The literature contains many mentions of other furan-functionalized systems such as styrene, acrylics, and polyurethane (Canary; Stevens 1992; Craven 1969; Goiti et al. 2004; Gousse et al. 1998; Laita et al. 1997; Loy et al. 2002; Stevens 1979). Future work will include applying the Diels-Alder chemistry to non-epoxy networks and evaluating their healing ability.

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